We report here the first occurrence of berthierine-bearing flint clays, one Ordovician and one Pennsylvanian in age. They are characterized by a berthierine-kaolinite-boehmite (bkb) assemblage. The Pennsylvanian flint clay from northeastern Kentucky is more typical in that it occurs in association with coal measures.

The Ordovician occurrence from northwestern Illinois is the oldest flint clay of which we are aware. Because it is Ordovician, it formed before the evolution of terrestrial vascular plants. All previous reports of flint clays point to a genetic connection between flint-clay formation and the growth and decay of plants (Bohor and Triplehorn, 1993). Except for the high berthierine content and greenish color, the physical properties of this flint clay are similar to those of other kaolinitic flint clays. Some samples of the Ordovician flint clay are nearly pure berthierine.

The Ordovician flint clay is a facies of the Neda Formation (~440 Ma), the uppermost formation of the Ordovician Maquoketa Group, which, in northern Illinois, northeastern Iowa, and southern Wisconsin, is unconformably overlain by Silurian carbonates. This unconformity is exposed in a narrow northwest-southeast corridor in the vicinity of the twin cities of Sterling and Rock Falls, Illinois. This corridor was formed between two glacial till sheets, one deposited by an Illinoian glacier that reached its southern limit to form the north side of the corridor, and the other by another lobe of Illinoian ice that pushed generally to the southwest so the northern edge of this tongue forms the southern margin of the corridor (Figure 1).

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Soils that formed on the marine Maquoketa Group after retreat of the Ordovician seas now constitute the Neda Formation (Yapp, 1993). Invasion of Silurian seas deposited carbonate rocks trapping this paleosol in those places where it had not eroded away. This marine transgression completed the sub-Tippecanoe II unconformity (Buschbach and Kolata, 1990). In the central United States, the Neda Formation is composed of calcareous oolites at some outcrops and goethitic or hematitic oolites at others. The Fe-oxide oolites occur in a few small localized places in northern Illinois, northeastern Iowa, and southeastern Wisconsin and are composed of ~0.1-3 mm, flattened, concentrically layered, elliptical spheroids or ooids containing chiefly goethite, calcite, kaolinite, and argillaceous dolomite.

In southeastern Wisconsin, these rocks have been mined as Fe ore (Kolata and Graese, 1983; Witzke and Heathcote, 1983; Khiessendorf, 1991). Apparently the calcareous oolites were replaced by goethite, most likely as a pedogenic process.

Only in the Sterling-Rock Falls area has the Neda Formation been found as a berthierine-rich flint clay facies. Even here, rapid lateral mineralogical changes indicate that the berthierine-rich flint clay facies is confined to a small area. Lateral changes within short distances are reflected by two locations, one a drill hole in the city of Sterling and one a few kilometers...
south. In both, at approximately the stratigraphic level of the Neda Formation, claystones are predominately soft, dispersible fireclay-type kaolinite (Hughes et al., 1993). The kaolinite in the berthierine-rich flint clay is well crystallized compared to fireclay-type kaolinite and the kaolinite in goethite-dominated zones (Hughes et al., 1993) of the Neda Formation. Clays composed of well-crystallized kaolinite + hematite found in the Sterling area appear to be a product of weathering of berthierine-bearing flint clays.

Optical petrography and scanning electron microscopy (SEM) using energy dispersive X-ray (EDX) analysis of 0.5–3-mm ooids or ellipsoidal bodies in the Sterling pipestone show roughly concentric structures and, in some cases, fragments of concentric shells as nuclei that may be from reworked ooliths. Thin sections of the Sterling pipestone and the Ohio pipestone are superficially similar but differ in details when examined closely (Figure 2). In the Sterling pipestone, SEM/EDX analyses show that boehmite, and to a lesser extent kaolinite, tend to be concentrated in the ooids. The ooliths vary in amount from sample to sample from almost zero to abundant. We have one sample with almost no ooliths and we refer to this one as massive. There seems to be an approximate relation between the amount of ooliths and the amount of boehmite and extent kaolinite. The original calcareous ooliths were apparently replaced by boehmite and kaolinite. The ooids in the Ohio pipestone, in contrast, are structureless except for an outermost ring. Some of the kaolinite in Ohio pipestone has a vermicular habit, a habit not found in the Sterling pipestone.

Brindley (1982) stated that the physical and chemical characteristics of berthierine are not easily studied for three reasons. It occurs in heterogeneous specimens, it is easily confused with chamosite, especially if small amounts of clinochlore are present, and ortho-
rhombic and monoclinic polytypes commonly exist together (Guthrie and Bish, 1992). In addition, the X-ray tracing of berthierine is very similar to that of kaolinite. Hence, berthierine has only rarely been reported. Once its presence is considered, it is differentiated on X-ray diffraction tracings from kaolinite because the 001 peaks of the two minerals are different enough to form either shoulders or an anomalously broad peak. The 002 peaks are usually far enough apart to be resolved into separate peaks (Figure 3). Berthierine also can be distinguished from kaolinite because it decomposes on heating in the range from 300 to 400°C, well below the range for the breakdown of kaolinite. Unlike chamosite, which if present in small amounts will have a barely discernible peak at 14 Å, but which will increase in intensity upon heating to 550°C, berthierine does not have any peak at 14 Å, heated or not. With increased awareness of this mineral, we predict that berthierine will be more commonly recognized in flint clays.

Brindley (1982) could present only 14 analyses of berthierine from the literature. These ranged from ~12

to 30 wt. % $\text{Al}_2\text{O}_3$. Berthierine in the average Sterling pipestone has ~30 wt. % $\text{Al}_2\text{O}_3$ (Table 1). It is noteworthy that some berthierines contain $^{\text{IV}}\text{Al} \cong \text{Si}$. Wetchemical (J.W. Stucki, unpubl. data, 1995) and Mössbauer-spectroscopy determinations (J.W. Stucki, unpubl. data, 1995) of our massive Sterling pipestone sample indicate that ~8 wt. % of iron is Fe$^{3+}$. Iron in the average berthierine-rich Sterling pipestone is concentrated in berthierine, but may rarely occur along oxidized fractures in goethite. Sequential acid-dissolution analyses of the berthierine in our samples (in 1 N HCl) followed by inductively coupled plasma (ICP) analysis (Hughes and Moore, 1997) show that berthierine also contains ~0.4 wt. % Li. Addition of this Li to the structural formulas of Brindley (1982) fully fills the ~0.2 vacant octahedral sites that Brindley needed to balance the formula unit. Using the method of Brindley (1982) and adding the Li, the structural formula of berthierine in our massive sample is:

$$(\text{Fe}^{2+}_{1.8}\text{Al}_{0.87}\text{Fe}^{3+}_{0.16}\text{Mg}_{0.15}\text{Li}_{0.06})(\text{Si}_{0.95}\text{Al}_{1.05})\text{O}_4(\text{OH})_4.$$  

Lower Pennsylvanian flint clay from the Olive Hill Clay Bed (Patterson and Hosterman, 1960; Wanless, 1975; Smyth, 1984; Rice et al., 1994) also contains the bkb assemblage with a few samples containing ≤50% berthierine. Sequential-dissolution analysis showed that the berthierine in two samples from Kentucky contained about the same amount of Li as in the berthierine from the Sterling pipestone. Also like the Sterling pipestone, boehmite occurrence in the Olive Hill flint clay is sporadic, and may be present mainly in ooliths.

We suggest three hypotheses for forming this berthierine-rich flint: 1) Fe-oxide-rich red earths and fire clays developed as upland soils with well-oxygenated and well-drained profiles, while flint clays formed below the water table at the base of drained soils or in lowland areas; 2) flint clays formed by selective diagenesis of a widespread soil of Fe-oxide-rich red earths and fireclays during advance of the Silurian seas; and 3) flint clays were the product of diagenesis after burial, either by simple burial or a combination of burial and hydrothermal alteration.

Table 1. Comparison of the composition of two Sterling pipestones, Ohio pipestone, and Brindley's berthierines, in wt. %.

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>TiO$_2$</th>
<th>P$_2$O$_5$</th>
<th>Trace Elements</th>
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<tbody>
<tr>
<td>Massive Sterling$^{2,3}$</td>
<td>23.64</td>
<td>29.01</td>
<td>35.20</td>
<td>0.17</td>
<td>1.68</td>
<td>0.16</td>
<td>0.10</td>
<td>1.46</td>
<td>0.31</td>
<td>8.26</td>
</tr>
<tr>
<td>Oolitic Sterling$^{2,3}$</td>
<td>25.91</td>
<td>31.26</td>
<td>29.22</td>
<td>0.23</td>
<td>1.29</td>
<td>0.13</td>
<td>0.13</td>
<td>1.49</td>
<td>0.60</td>
<td>9.74</td>
</tr>
<tr>
<td>Ohio pipestone$^4$</td>
<td>44.31</td>
<td>38.07</td>
<td>2.02</td>
<td>0.09</td>
<td>0.18</td>
<td>0.22</td>
<td>0.11</td>
<td>1.34</td>
<td>0.16</td>
<td>13.51</td>
</tr>
<tr>
<td>Brindley's (1982)$^4$</td>
<td>23.25 ± 2.34</td>
<td>22.08 ± 4.48</td>
<td>38.01 ± 2.38</td>
<td>3.45 ± 2.30</td>
<td></td>
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$^1$ LOI, loss-on-ignition of berthierine-containing samples is in error due to oxidation of Fe$^{2+}$ to Fe$^{3+}$, with weight gain.
$^2$ Analysis of bulk samples by X-ray fluorescence (XRF).
$^3$ Analysis by selective dissolution and ICP of the berthierine in these and in two samples of Olive Hill flint clay each yielded ~0.4 wt. % Li.
$^4$ Average of 14 samples and the first standard deviation.
In support of the first hypothesis, preservation of oolith structure and the regional distribution of red-earth pipeclays and flint clays suggest that the Sterling pipestone formed during pedogenesis in poorly oxygenated lowland areas or in the parts of well-drained soil profiles that were below the water table, or both. Yapp (1993) concluded that the Neda Formation was formed in a subaerial weathering environment, but found no berthierine in his samples. Based on a reinterpretation of data from Smyth (1984) and on samples we collected, we recognized berthierine-containing flint clays restricted to near the base of the flint-clay zones in the Olive Hill Clay Bed in eastern Kentucky. This suggests that berthierine formed below the oxygenated zone in these paleosols. The high Fe content of the Neda Formation strongly suggests that it formed as a laterite, which is appropriate for a region that was ~10° south of the equator in Late Ordovician time (Van der Roo, 1988). In addition, boehmite, when present in non-marine settings, is commonly associated with the intense weathering that produces bauxites (Hsu, 1989).

Fritz and Toth (1997) and Toth and Fritz (1997) provide support for the second hypothesis, selective diagenesis. They suggested that marine transgression may provide the conditions for transforming Fe oxides to berthierine by imposing low-Eh conditions on in situ or reworked lateritic material. In support of the third hypothesis, hydrothermal alteration, Kean (1981) suggested that some original goethite in the Neda Formation was altered to hematite by dehydration ~320 Ma. Grathoff and Moore (1996) concluded that diagenetic illites of the Maquoketa Group shales and the Waukesha illite (Grathoff et al., 1995) also formed at this time as the result of an episode of hydrothermal fluid movement through the Illinois Basin. The occurrence of significant amounts of Li in the berthierine, the presence of boehmite rather than gibbsite, and the detection of probable diagenetic illite and K-rich feldspar suggest that the original pedogenic mineral suite was at least partially altered by post-burial diagenesis.

Assemblages of iron oxides, siderite, and chamsoite or berthierine are common in oolitic iron ores. Maynard (1986) found berthierine predominates in younger deposits, whereas Paleozoic ores contain only chamsoite. He suggested that chamsoite is a late diagenetic transformation product of berthierine. We have not been able to reconcile the genesis of the Sterling pipestones with the conclusions of Maynard.

This first report of bkb flint clays of such different ages should help us better understand how berthierine is developed in flint clays and how flint clays form in general. In these two cases, one flint clay formed before and one after the evolution of vascular land plants. Berthierine and kaolinite have the same 1:1 structure, which suggests that these 1:1 clay minerals are interchangeable in forming flint clays. Berthierine, however, contains a greater range of minor and trace-element substitutions than kaolinite. The Pennsylvanian-age flint clay appears to have formed in the conventional manner. The Ordovician one most likely formed as a laterite (hypothesis 1) and was later altered to form berthierine (hypothesis 3). From a geological standpoint, the puzzle of how the Neda Formation can be formed of goethitic ooliths in one place, berthierine flint clay in another, and fireclay-type kaolinite in yet another is still unresolved. Clearly the lateral mineralogical variations of the Neda Formation need to be better documented and explained.

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